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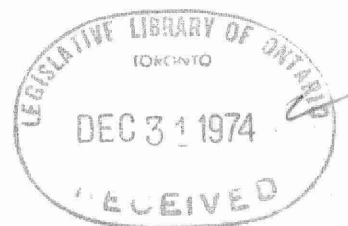
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CHEMICAL ANALYSIS FOR EVALUATION OF
SOIL SORPTION PROPERTIES

Pollution Control Planning Branch
Ministry of the Environment

October, 1974.



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CHEMICAL ANALYSIS FOR EVALUATION OF
SOIL SORPTION PROPERTIES

by

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Applied Sciences Section
Pollution Control Planning Branch
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TABLE OF CONTENTS

	<u>Page No.</u>
Introduction	
1. Sample Preparation	1
1.1 Sample Reception	1
1.2 Drying Soils	1
1.3 Grinding and Sieving	1
1.4 Sample Storage	2
2. Determination of Moisture Content	3
3. Soil pH	4
3.1 Soil Paste Technique	4
3.2 Potassium Chloride Technique	5
4. Lime Potential	6
4.1 Analytical Technique	6
5. Soluble Salts	7
5.1 Determination of Total Salinity	7
5.2 Determination of Individual Soluble Ions	8
6. Phosphate Analysis	10
6.1 Total Phosphate	10
6.2 Total Inorganic Phosphate	11
6.3 Total Organic Phosphate	11
7. Ion Exchange Capacity	12
7.1 Cation Exchange Capacity	12
7.2 Anion Exchange Capacity	14
8. Sorption Isotherm Analysis	15
8.1 Analytical Techniques	15

INTRODUCTION

The movement of contaminants through soil poses a major difficulty in the design and planning of private waste treatment systems. The problems connected with waste treatment using tile field systems require knowledge of the capacity or degree of uptake of specific contaminants by the soil, the effect of concentration, and the rate of movement. To evaluate the capabilities of soils for contaminant removal, the analyses and technique described on the following pages will be useful in this respect. Of the techniques described, the soil adsorption isotherm determination is the most informative for determining soil capacities for single and multi species systems and the concomitant effects of varying concentration. The rate of contaminant movement can then be calculated using the isotherm parameters.

1. SAMPLE PREPARATION

1.1 Sample Reception

Each batch of soil samples arriving at the laboratory should be accompanied or preceded by an explanatory letter or the official Ministry Lab Analysis form giving relevant field data and indicating the analyses required. Every individual sample should be labelled unambiguously with its field number.

Sample information is then to be entered into a ledger and each sample given a lab number. A particle size analysis is a necessary requirement for each sample before chemical analysis.

1.2 Drying of Soils (1)

The soils are emptied from their containers and spread to dry on flat trays, 50 x 60 cm, and 2.5 cm deep. Identification must be maintained at this stage by labelling the tray or placing a plastic tag in the soil. The soils are then allowed to dry in the air at conditions not exceeding 35 C, and relative humidities between 30 and 70%.

1.3 Grinding and Sieving

Once the sample is dried, stones and pieces of macro-organic matter are picked out and, if necessary, weighed. The remainder of the sample is then crushed and sieved. Large lumps are broken up by hand and then the soil sample is ground gently with a wooden roller.

After grinding, part of the soil should be screened for particle size distribution. For most routine chemical analyses, the remainder of the soil is screened through a 2 mm (10 mesh) sieve to give what is referred to as the 2-mm fine

earth. Finer particle sizes may be required for micro or semi-micro analyses.

1.4 Sample Storage

The ideal container for a soil sample is a screw-capped glass jar which should be clearly labelled with the laboratory number and the degree of fineness of the sample. Although plastic containers are popular because they are cheaper and less breakable than glass, investigations have revealed that soil samples may undergo certain fundamental changes in clay minerals. In the case of montmorillonite clays in soils, organic compounds may pass from the plastic to the clay mineral.

2. DETERMINATION OF MOISTURE CONTENT⁽¹⁾

Knowledge of moisture content may be necessary for the calculation of other analytical results. Some soils may lose weight on heating as a result of the decomposition of organic matter but this is not considered to be a serious source of error.

Approximately 5 gm soil are accurately weighed into a tared tin and then dried in an electric oven at a temperature of 105 - 110 C for 8 hrs. After cooling in a dessicator the loss in weight is determined.

3. SOIL pH⁽¹⁾

The measurement of pH gives information about associated soil properties such as phosphorus availability, base status, etc. The more acid the soil, the more mobile elements such as iron, manganese, copper, and other minor elements will become. The degree of acidity is critical when considering phosphate fixation capacity. The rapidity with which phosphate is fixed by very acid soils is due to the secondary effects of iron and aluminium liberation.

As soils normally contain salts, the suspension is strictly a system of soil particles in salt solution and the effect of diluting is to reduce the salt concentration.

A further effect of measuring soil pH is the fact that the pH value of a soil paste will be different from that of its supernatant liquid, due to a hydrogen ion gradient. This is due to the effect of the electric double layer. One way of destroying the double layer effect and obtaining the same pH in the supernatant liquid as for the soil paste is to add an excess of salt, usually potassium chloride.

3.1 Soil Paste Technique

3.1.1 Preparation

Spread the 2-mm fine earth on a sheet of polyethylene and snatch-sample to obtain a representative sample of the required size.

3.1.2 Paste Technique

Place about 200 gm of the soil in a suitable container and add distilled water while stirring with a spatula. Occasionally tap the container on the bench to consolidate the mass.

Initially add sufficient water to bring the soil to near saturation as this gives better results than a slow gradual addition.

At saturation, the soil surface glistens, the soil flows slightly if the container is tipped and it easily slides off the spatula. Allow to stand 1 hour.

Measure pH by inserting the electrodes into the soil paste and move the electrodes to insure good contact and read the pH.

3.2 Potassium Chloride Technique

Snatch-sample 10 gm of soil and mix in a beaker with 25 ml of 1M KCl solution (75 gm/l KCl), and allow the mixture to stand for 1 hour before measuring pH.

4. LIME POTENTIAL ⁽¹⁾

Because of the problems involved in measuring the pH of soil suspensions due to the varying single ion activity, a more suitable measurement is the ratio of ionic activities which are relatively constant and characteristic for a soil.

For a soil in equilibrium with a calcium solution the ratios of the activities are constant

i.e.

$$\frac{a_{H^+}}{(a_{Ca^{2+}})^{\frac{1}{2}}} = k$$

or

$$pH - \frac{1}{2} pCa = k$$

This is the lime potential of which the value is independent of the calcium - magnesium ratio; it is less affected by soil concentration and moisture than is pH, and is more characteristic of the soil.

4.1 Analytical Technique

Reagent: Calcium chloride solution, 0.01 M:

about 1.3 gm $CaCl_2$ (anhyd.) is dissolved in water and the solution diluted to 1 litre. Standardize with EDTA and dilute to exactly 0.01M.

Procedure: Shake 10 gm of 2-mm soil with 20 ml of $CaCl_2$ for 30 min and measure pH.

∴ Lime Potential = measured pH - 1.14

5. SOLUBLE SALTS⁽¹⁾

The main source of the soluble salts which are present to some extent in all soils is the primary minerals. Of the soluble anions, sulphate and chlorides predominate, but exchangeable cations in equilibrium with carbonic acid in the soil give rise to soluble carbonates and bicarbonates. Nitrates, phosphates and silicates occur in varying amounts, often negligible but sometimes predominant.

The cations involved are usually calcium, magnesium, potassium and sodium, although other cations become more important in certain kinds of soils; e.g. aluminium, iron and manganese in acid soils.

When a soil has excess soluble salts it is said to be saline. In the U.S.D.A. handbook (No. 60) on salinity, a saline soil is defined as one having a conductivity (of saturation extract) greater than 4 mS cm^{-1} * (4 millimhos/cm) at 25°C , a soluble sodium content of less than half of the total soluble cations and a pH value usually less than 8.5.

5.1 Determination of Total Salinity

5.1.1 Soil Paste Technique

The soil paste is prepared as in Section 3.1.2. Filter with a Buchner funnel, then filter the filtrate using a millipore filter. Determine conductivity of the filtrate using an appropriate conductivity meter and record the temperature.

* milliSiemens/cm - SI units

5.1.2 Preparation of a 1:5 extract

Weigh 20 gm of 2-mm soil into a 250 ml erlenmyer flask and add 100 ml of distilled water. Stopper the flask and shake for 30 minutes, then allow to stand for 15 minutes to let the bulk of the soil settle. Centrifuge to remove most of the suspended matter and filter through a millipore filter. Determine conductivity of the filtrates and correct for temperature.

5.1.3 Calculations

The soil paste value can be converted into salt concentration in gm/litre using Figure 1. The 1:5 extract values can be converted to % total soluble salts using the equation;

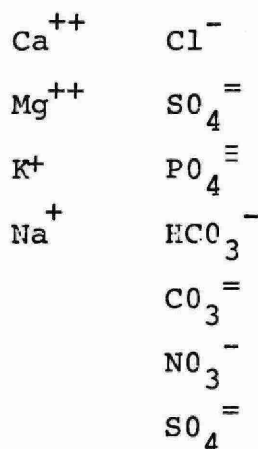
$$\% \text{ total soluble salts} = 336 \times K_{25}$$

where K_{25} is conductivity in mS cm^{-1} , or, for units of milliequivalents/100 gm the following equation may be used:

$$\text{salts, meq/100 gm} = 5 \times K_{25}$$

5.2 Determination of Individual Soluble Ions

Individual ions normally determined are



These ions are analyzed from the filtrates obtained in sections 5.1.1 and 5.1.2. The techniques used for the determinations are those recommended in "Standard Methods".⁽²⁾ Newer techniques are also applicable provided interference with other ions is negligible or can be corrected for.

6. PHOSPHATE ANALYSIS

Phosphorus occurs in soils in organic and inorganic forms, the relative proportions of which vary with organic matter content but usually the organic form predominates. Phosphorus tends to accumulate in the finer fractions of soil and these increase as the clay content increases.

Most soil determinations involve two distinct steps; preparation of a solution containing the phosphorus, and then, a quantitative analyses of the phosphorus content. Colormetric methods forming molybdenum blue appear to be the most sensitive technique for soil extracts containing small amounts of P.

6.1 Total Phosphate⁽¹⁾

6.1.1 Digestion with Perchloric-nitric Acids

Accurately weigh about 1.0 gm of oven-dry, 0.15 mm soil into a 250 ml tall-form beaker and add 20 ml of concentration nitric acid. Cover the beaker and cautiously heat to oxidize organic matter. Add 10 ml of 60% perchloric acid and digest the mixture (using a Speedy-vap cover) until dense white fumes of acid appear. Use a little extra perchloric acid to wash down the sides of the beaker as necessary.

During the evaporation of the digest there is no need to drive off completely the perchloric acid; take up the filtered digest in dilute hydrochloric acid and dilute to 100 ml.

6.1.2 $\text{PO}_4^{=}$ Analysis

Analyze aliquots of digest for phosphates according to "Standard Methods" using the stannous chloride - molybdate method.

6.2 Total Inorganic Phosphorus

Reagent: concentrated hydrochloric acid

Procedure: Weigh 1 gm of <0.5 mm air-dry soil into a centrifuge tube and mix with 10 ml of hydrochloric acid. Heat on a steam-bath for 10 minutes and then add a further 10 ml of acid. Allow to stand at room temperature for 1 hour, add 50 ml of water and centrifuge. Decant the solution into a 250 ml volumetric flask and make to volume.

Determine the phosphorus in solution immediately by the method in Section 6.1.1, in order to prevent errors arising from hydrolysis.

6.3 Total Organic Phosphorus

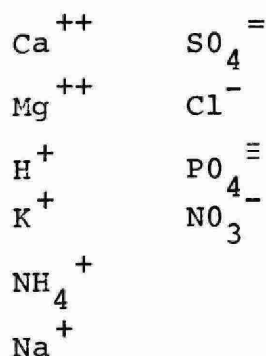
Weigh 1 gm of <0.5 mm air-dry soil into a silica crucible and heat at 240°C for 1 hour in an electric muffle furnace. When cool, transfer the ignited soil to a 100 ml centrifuge tube. A second 1 gm sample of soil is weighed directly into another centrifuge tube.

The procedure is then exactly as in Section 5.2 for total inorganic phosphorus and the difference between the phosphorus found in ignited soil and non-ignited soil is a measure of total organic phosphorus.

7. ION EXCHANGE CAPACITY^(1, 3, 4)

Ion exchange is the reversible process by which cations and anions are exchanged between solid and liquid phases in a stoichiometric manner. Clay minerals have the property of holding ions in an exchangeable state. The exchangeable ions are held around the outside of the silica-alumina clay - mineral matrix and the exchange reaction does not affect the silica-alumina structure. The exchange capacity may be expressed in units of milligrams per 100 grams or more generally as milliequivalent weights per 100 grams (meq/100 gm).

In clay minerals, the exchangeable ions are:



The conventional methods for determining exchange capacity involve saturating the soil with an index ion, washing out the excess, and determining the amount of ion retained.

7.1 Cation Exchange Capacity

Using sodium as index ion; this technique provides a rapid method sufficiently accurate for routine work provided that due care is taken to ensure adequate dispersion and shaking of the sample.

Reagents: Sodium acetate solution, 1.0 M: 136 gm/l sodium acetate trihydrate and adjusted to pH 8.2.

Ammonium acetate solution, 1.0 M: add 57 ml glacial acetic acid and 68 ml of strong ammonium hydroxide to 800 ml of water. Dilute to 1 l and adjust to pH 7.0.
Magnesium acetate solution, 0.5 M: 107 g/l crystalline salt.

Procedure: Weigh 5 gm of 2-mm soil into a 50 ml centrifuge tube, add 30 ml of sodium acetate solution and shake for 5 minutes. The tubes should be stoppered with polyethylene or clean rubber stoppers and not corks which introduce errors. Centrifuge the tubes at 200 rev/s for about 5 minutes until the supernatant liquid is clear. Decant and discard the liquid and repeat the shaking and centrifuging four times more with fresh portions of acetate solution. Shake the soil with 30 ml of 95% ethanol for 5 minutes, centrifuge and discard the liquid. Repeat the ethanol washing three times. Finally extract the soil with three 30 ml portions of magnesium acetate solution and collect the extracts in a 100-ml graduated flask. Occasionally it is necessary to filter the extracts after centrifuging.

Dilute the combined extracts to 100 ml and determine the sodium content.

Note: Some soils become sticky during the saturation process and it is extremely important to ensure complete re-dispersion in the next added solution. For soils giving difficulty in this respect it may

be better to use a leaching technique.

Calculation:

$$\text{C.E.C. meq/100 gm soil} = \frac{10 \times \text{Na concentration in meq/l}}{\text{weight of sample}}$$

7.2 Anion Exchange Capacity

Reagents: Triethanolamine solution: Dilute 45 ml of triethanolamine to 500 ml and adjust to pH 8.1 with HCl. Dilute to 1.0 l and mix with 1.0 l of water containing 50 gm $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. Calcium chloride solution: 50 gm/l $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, adjusted to pH 8.0 with saturated $\text{Ca}(\text{OH})_2$ solution. Ammonium fluoride in Hydrochloric acid: 0.03 M NH_4F (1.11 gm NH_4F) in 0.025M HCl (0.912 gm HCl in 1 l).

Procedure: Leach 10 gm of 2-mm soil with 100 ml of triethanolamine solution and wash six times with 95% ethanol. Leach the soil with 100 ml of calcium chloride solution and again wash. Dry the calcium-saturated soil at 45°C and weigh into an erlenmyer flask a sufficient quantity to give 0.2 meq. C.E.C. Add 20 ml of phosphoric acid solution and shake for 30 minutes. Filter with a millipore filter and take a 1 ml aliquot of liquid to determine phosphorus. In a separate 1 gm sample of soil, extract the phosphorus with 8 ml of ammonium fluoride-hydrochloric acid solution and determine its content.

Calculation

$$\text{A.E.C. meq/100 gm soil} = (\text{extractable P} + \text{P adsorbed}),$$

expressed as meq/100 gm soil.

8. SORPTION ISOTHERM ANALYSIS^(3,4)

Because of the ion exchange and adsorption-desorption properties of soils, the degree of sorption will vary with the solution concentration according to Le Chatelier's law. Equilibrium between soils and solutions can be described by rigorous thermodynamics which is quite general and requires no mechanisms or model to describe the phenomena. Because the thermodynamic treatment yields minimal information, empirical models are more practical and are easier to handle.

A convenient model for soil sorption analysis is the well-known Langmuir Model which relates the amount absorbed to the solution equilibrium concentration: i.e.

$$\frac{x}{m} = \frac{\bar{Q}bc_e}{1+bc_e}$$

where x is the weight of ion adsorbed, m is the weight of soil, C_e is the equilibrium concentration, b is an empirical constant, and \bar{Q} is the weight capacity of the soil for the species in question.

This equation thus relates the degree of adsorption to concentration in solution with remarkable accuracy. Experimental measurements of x/m and C_e allow the determination of the maximum soil capacity, \bar{Q} for the particular ion in question. In addition, with slight modifications, the above equation is applicable to multi-ion solutions.

8.1 Analytical Techniques

Reagents: 1 litre of standard solution of desired ion

eg. 5.0 mg/l PO_4^{3-}
75.0 mg/l Cl^-
75.0 mg/l NO_3^-

Reagents as required by technique in "Standard Methods".

Procedure: Weigh out accurately, approximately 1, 3, 5, 7 and 10 gram samples of soil passing 200 mesh (or 60 mesh, in the case of sand), into 250 ml erlenmyer flasks. Add 150 of standardized reagent, seal the flasks and shake for 24 hours. Allow to stand 1 hr, then centrifuge the supernatant to obtain 100 mls of solution. Filter through a millipore filter and analyze for the ion in question.

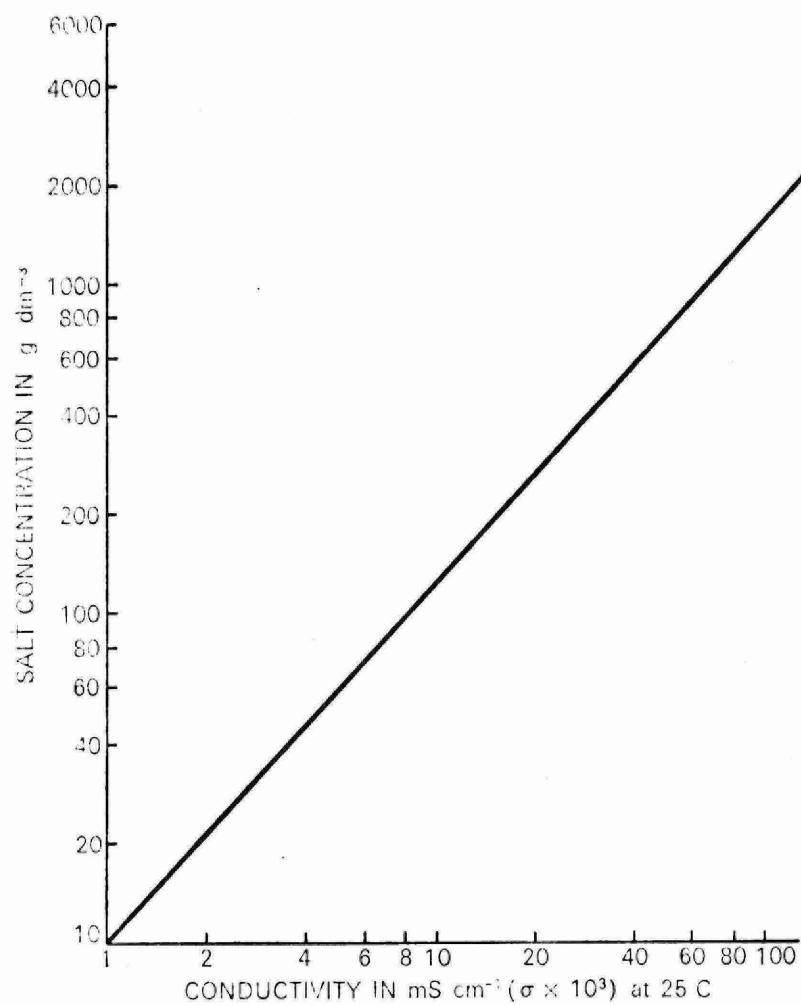


Figure 1. Relationship of concentration of saturated extracts of soils with electrical conductivity (USDA Handbook No. 60, US Salinity Laboratory).

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